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Analysis of Chemical Warfare Agents: General Overview, LC-MS Review, In- House LC-ESI-MS Methods and Open Literature Bibliography

P.A. D'Agostino and C.L. Chenier
DRDC Suffield

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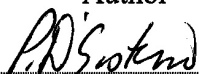
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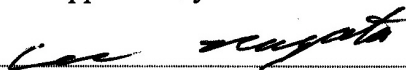
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Abstract

Ratification of the Chemical Weapons Convention by more than 165 States Parties has reduced the risk of chemical warfare agent use, but there still remains a concern that other parties may make use of these weapons against civilian or military targets. Concerns within the defence and homeland security communities over possible terrorist use as well as the requirements for a verifiable Chemical Weapons Convention, have driven the development of analytical methods such as liquid chromatography-mass spectrometry (LC-MS) for the detection and identification of chemical warfare agents. This paper provides a general overview of chemical warfare agents and analytical methods for their analysis, a focused review on LC-MS applications, a summary of in-house LC-MS methods developed at DRDC Suffield, and a comprehensive bibliography of analytical open literature papers dealing with chemical warfare agent detection and identification.

Résumé

La ratification de la Convention sur les armes chimiques par plus de 165 États parties a réduit le risque d'utilisation d'agents de guerre chimiques mais il existe encore l'inquiétude que d'autres parties utilisent ces armes contre des cibles civiles ou militaires. Cette inquiétude du milieu de la défense et de la sécurité de la nation au sujet d'une éventuelle utilisation terroriste ainsi que les exigences susceptibles de vérification de la Convention sur les armes chimiques ont entraîné la mise au point de méthodes analytiques telles que le couplage de chromatographie en phase liquide et spectrométrie de masse (CPL-SM) pour la détection et l'identification d'agents de guerre chimiques. Cet article procure une vue d'ensemble des agents de guerre chimiques et des méthodes analytiques pour leurs analyses, une étude ciblée des applications CPL-SM, un sommaire des méthodes internes CPL-SM mises au point à RDDC Suffield et une bibliographie compréhensive d'articles analytiques de source non classifiée traitant de la détection et de l'identification d'agents de guerre chimiques.

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Executive summary

Introduction: Ratification of the Chemical Weapons Convention by more than 165 States Parties has reduced the risk of chemical warfare agent use, but there still remains a concern that other parties may make use of these weapons against civilian or military targets. Concerns within the defence and homeland security communities over possible terrorist use as well as the requirements for a verifiable Chemical Weapons Convention, have driven the development of analytical methods such as liquid chromatography-mass spectrometry (LC-MS) methods for the detection and identification of chemical warfare agents.

Results: This paper provides a general overview of chemical warfare agents and analytical methods for their analysis, a focused review of LC-MS applications, a summary of in-house LC-MS methods developed at DRDC Suffield, and a comprehensive bibliography of analytical open literature papers dealing with chemical warfare agent detection and identification.

Significance: The review sections provide the homeland security and defence communities with an overview of chemical warfare agents and analytical methods for their determination. Researchers interested in developing new methods for chemical warfare agents may use the reviewed material to quickly ascertain the state of development of analytical methods, in particular LC-MS methods, for chemical warfare agents.

Future Plans: The reviewed materials will be used for reference purposes during the development of high field asymmetric waveform ion mobility spectrometry (FAIMS) mass spectrometry, a new analytical technique with the potential to rapidly separate and identify chemical warfare agents.

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Sommaire

Introduction : La ratification de la Convention sur les armes chimiques par plus de 165 États parties a réduit le risque d'utilisation d'agents de guerre chimiques mais il existe encore l'inquiétude que d'autres parties utilisent ces armes contre des cibles civiles ou militaires. Cette inquiétude du milieu de la défense et de la sécurité de la nation au sujet d'une éventuelle utilisation terroriste ainsi que les exigences susceptibles de vérification de la Convention sur les armes chimiques ont entraîné la mise au point de méthodes analytiques telles que le couplage de chromatographie en phase liquide et spectrométrie de masse (CPL-SM) pour la détection et l'identification d'agents de guerre chimiques.

Résultats : Cet article procure une vue d'ensemble des agents de guerre chimiques et des méthodes analytiques pour leurs analyses, une étude ciblée des applications CPL-SM, un sommaire des méthodes internes CPL-SM mises au point à RDDC Suffield et une bibliographie compréhensive d'articles analytiques de source non classifiée traitant de la détection et de l'identification d'agents de guerre chimiques.

Portée des résultats : Ces sections de l'étude procurent, au milieu de la sécurité de la nation et de la défense, une vue d'ensemble des agents de guerre chimiques et des méthodes analytiques visant à les déterminer. Les chercheurs intéressés à la mise au point de nouvelles méthodes pour les agents de guerre chimiques peuvent utiliser le matériel examiné pour vérifier rapidement l'état de la mise au point des méthodes analytiques, dont surtout les méthodes CPL-SM, concernant les agents de guerre.

Plans futurs : Les matériaux examinés seront utilisés comme référence durant la mise au point de la spectrométrie de masse de la spectrométrie de mobilité ionique de forme d'onde asymétrique de haute résolution (FAIMS), une nouvelle technique analytique ayant le potentiel de séparer et d'identifier rapidement les agents de guerre chimiques.

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General overview

Historical background

Chemical warfare agents [1-5] are toxic chemicals controlled by the Convention on the Prohibition of the Development, Production, Stockpiling and Use of Chemical Weapons and their Destruction (commonly referred to as the Chemical Weapons Convention or CWC). Poisonous or toxic compounds have been utilized in an effort to gain military superiority throughout history, but it is only during the past century that chemical warfare agents have been produced and used on a large scale. Tear gas grenades were used in 1914 by the French army at the outbreak of the First World War, but it was not until the German army used chlorine near Ypres in 1915 that the world entered the modern era of chemical warfare. Other chemical warfare agents such as phosgene and mustard were weaponized during the First World War and were used by both sides during the conflict.

Chemical warfare agent development and use continued following the First World War despite the signing of the 1925 Geneva Protocol, which banned the first use of chemical weapons. Mustard was used by the Italians against the Abyssinians (Ethiopia) during the 1936-1937 war and, just prior to the Second World War, the Germans discovered and produced the first nerve agent, tabun. Tabun was weaponized by the Germans but neither side made use of their chemical weapons stocks. More effective nerve agents, such as VX, were developed in the 1950's, mustard was used in the Yemen Civil War (1963-1967) and allegations of chemical warfare agent use were reported in South East Asian conflicts. Nerve and mustard agents were used by Iraq in the 1980's war between Iran and Iraq, and were considered a real threat to United Nations armed forces during their action against Iraq in 1991. Mustard and sarin were detected in samples collected in 1992 from a site where chemical weapons were thought to have been previously used against a Kurdish village. Most recently, sarin was released by the Aum Shinrikyo cult in the Tokyo underground transit system resulting in thousands seeking medical attention and twelve deaths.

The CWC was opened to signature in 1993, with the treaty coming into force on 29 April 1997. More than 175 States Parties have ratified the CWC and agreed not to develop, produce, stockpile, transfer or use chemical weapons and agreed to destroy their own chemical weapons and production facilities. A strong compliance monitoring regime involving site inspections was built into the CWC to ensure that the treaty remains verifiable. The Organisation for the Prohibition of Chemical Weapons, or OPCW, based in the Hague has responsibility for implementation of the treaty. Routine OPCW inspections have taken place at declared sites, including former CW production, storage and destruction sites, and challenge inspections could take place at sites suspected of non-compliance. Proliferation of chemical weapons and their use will hopefully decrease over the coming years as the OPCW proceeds towards its goal of world-wide chemical weapons destruction.

Concerns within the homeland security and defence communities over possible terrorist use as well as the requirements of a verifiable CWC, have driven the development and application of analytical methods for the detection and identification of chemical warfare agents [6].

Analytical techniques play an important role in this process as sampling and analysis will be conducted to ensure treaty compliance, to investigate allegations of use and to verify the use of these weapons for forensic purposes.

Chemical warfare agent categories

Chemical warfare agents have been classified into nerve, blister, choking, vomiting, blood, tear, and incapacitating agent categories based on their effect on humans. The most significant chemical warfare agents in terms of military capacity and past use are the nerve and blister agents. For these reasons the analysis of these compounds will be emphasized over the other groups in this review. The choking, blood, and vomiting agents, generally considered obsolete chemical agents, were employed during the First World War. The tear agents were used during the Vietnam War but their primary use, because of their inability to produce high casualties, remains in riot control and training.

Table 1 lists common chemical warfare agents, with their Chemical Abstracts registry numbers. It has been estimated that more than 10,000 compounds are controlled under the CWC, although in practical terms the actual number of chemical warfare agents, precursors and degradation products that are contained in the OPCW database is in the hundreds. The structures of common nerve and blister chemical warfare agents and their hydrolysis products are illustrated in Figure 1.

Table 1. Common chemical warfare agents

a) Nerve (reacts irreversibly with cholinesterase which results in acetylcholine accumulation, continual stimulation of the body's nervous system and eventual death)

<u>Full Name (Trivial Name(s))</u>	<u>CAS No.</u>
1-Methylethyl methylphosphonofluoridate (sarin, GB)	107-44-8
1,2,2-Trimethylpropyl methylphosphonofluoridate (soman, GD)	96-64-0
Cyclohexyl methylphosphonofluoridate (GF)	329-99-7
Ethyl dimethylphosphoramidocyanidate (tabun, GA)	77-81-6
O-Ethyl S-(2-diisopropylaminoethyl) methylphosphonothiolate (VX)	50782-69-9

b) Blister (affects the lungs, eyes and produces skin blistering)

<u>Full Name (Trivial Name(s))</u>	<u>CAS No.</u>
Bis(2-chloroethyl)sulfide (mustard, H)	505-60-2
Bis(2-chloroethylthio)ethane (sesquimustard, Q)	3563-36-8
Bis(2-chloroethylthioethyl)ether (T)	63918-89-8
Tris(2-chloroethyl)amine (HN-3)	555-77-1
(2-chloroethenyl)arsonous dichloride (lewisite, L)	541-25-3

c) Choking (affects respiratory tract and lungs)

<u>Full Name (Trivial Name(s))</u>	<u>CAS No.</u>
Chlorine	7782-50-5
Phosgene (CG)	75-44-5

d) Vomiting (causes acute pain, nausea and vomiting in victims)

<u>Full Name (Trivial Name(s))</u>	<u>CAS No.</u>
Diphenylarsinous chloride (DA)	712-48-1
10-Chloro-5,10-dihydrophenarsazine (adamsite, DM)	578-94-9
Diphenylarsinous cyanide (DC)	23525-22-6

e) Blood (prevents transfer of oxygen to the body's tissues)

<u>Full Name (Trivial Name(s))</u>	<u>CAS No.</u>
Hydrogen cyanide (HCN, AC)	74-90-8

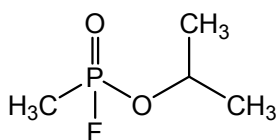
f) Tear (causes tearing and irritation of the skin)

<u>Full Name (Trivial Name(s))</u>	<u>CAS No.</u>
[(2-chlorophenyl)methylene]propanedinitrile (CS)	2698-41-1
2-Chloro-1-phenylethanone (CN)	532-27-4
Dibenz[b,f][1,4]oxazepin (CR)	257-07-8

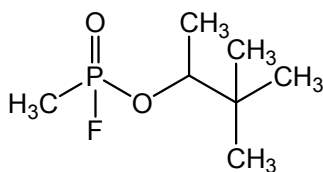
g) Incapacitating (prevents normal activity by producing mental or physiological effects)

<u>Full Name (Trivial Name(s))</u>	<u>CAS No.</u>
3-Quinuclidinyl benzilate (BZ)	6581-06-2

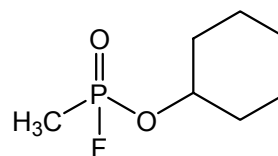
Nerve Agents



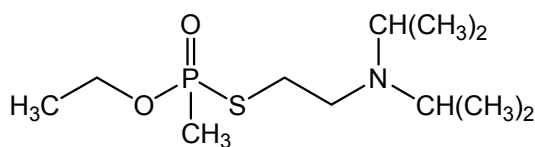
Sarin (GB)



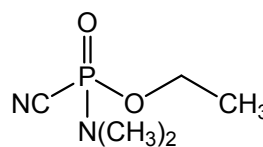
Soman (GD)



Cyclohexyl Sarin (GF)

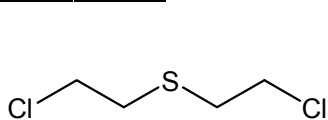


VX

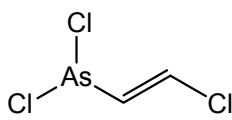


Tabun (GA)

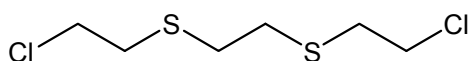
Blister Agents



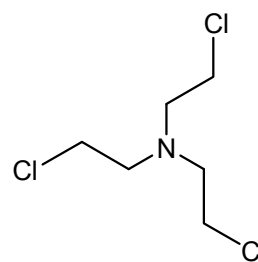
Mustard (H)



Lewisite (L)

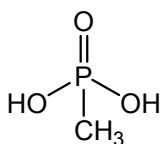


Sesquimustard (Q)

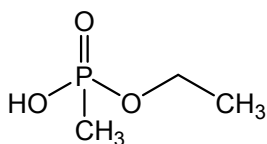


Nitrogen Mustard (HN-3)

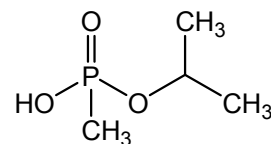
Hydrolysis Products



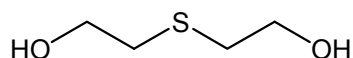
Methylphosphonic acid



Ethyl methylphosphonic acid



Isopropyl methylphosphonic acid



Thiodiglycol

Figure 1. Structures of common chemical warfare agents and their hydrolysis products.

Identification methods

Chemical warfare agents have often been referred to as warfare gases, but in fact many chemical warfare agents exist as liquids at ambient temperatures. The common chemical warfare agents have varying degrees of volatility and pose both a vapor hazard as well as a liquid contact hazard. This physical characteristic has made the analysis of chemical warfare agents amenable to the analytical techniques commonly employed for most environmental analyses, namely gas chromatography (GC) and liquid chromatography (LC) with a variety of detectors including mass spectrometry (MS) [7-10]. Synthetic or relatively pure samples not requiring chromatographic separation are also frequently characterized by nuclear magnetic resonance (NMR) or Fourier transform infrared (FTIR) spectroscopy.

The OPCW inspectorate, an important end user of analytical techniques for chemical warfare agents, requires the use of two or more spectrometric techniques and the availability of authentic reference standards for the unambiguous identification of controlled compounds. For this reason, the combined use of GC-FTIR has received increased attention, as newer technologies have led to detection limits approaching those routinely reported during GC-MS analysis. For analyses involving low levels of chemical warfare agents in the presence of high levels of interfering chemical background, tandem mass spectrometry (MS/MS) is often employed.

Chromatography

Contaminated samples containing chemical warfare agents typically contain multiple components that are best characterized following chromatographic separation. These samples usually fall into one of the following general categories; a) munitions or munition fragments (e.g., neat liquid or artillery shell casing), b) environmental (e.g., soil, water, vegetation or air samples), c) man-made materials (e.g., painted surfaces or rubber) and d) biological media (e.g., blood or urine). The ease of analysis depends on the amount of sample preparation required to obtain a suitable sample or extract for chromatographic analysis. In the simplest case where neat liquid can be obtained, the sample requires dilution with a suitable solvent prior to analysis. Environmental and other samples generally require (at a minimum) solvent extraction and concentration prior to analysis.

The most frequently employed analytical separation method for the screening of samples contaminated with chemical warfare agents is capillary column GC [9]. Separation of chemical warfare agents may be achieved with many of the commercially available fused silica columns coated with polysiloxane or other films and retention index data relative to n-alkanes and alkylbis(trifluoromethyl)phosphine sulfides (M-series) have been reported for many chemical warfare agents and related compounds. In general, the best separations have been achieved with moderately polar films such as (86%)-dimethyl-(14%)-cyanopropylphenyl-polysiloxane. Chiral stationary phases have also been developed for the resolution of stereoisomers of several chiral nerve agents, most notably soman. The use of multiple columns of differing polarity during one analysis has been successfully employed during chemical warfare agent analysis and the term "retention spectrometry" was coined to describe this technique.

Most of the GC detectors commonly applied to pesticide residue analysis have also been applied to the screening of samples for chemical warfare agents with detection limits typically being in the nanogram to picogram range. Flame ionization detection (FID) is routinely used for preliminary analyses as this technique provides a good indication of the complexity of a sample extract. Figure 2 illustrates typical GC-FID chromatographic separations obtained for three different munitions-grade mustard formulations, HT, HS and HQ, each of which contain mustard and a number of related longer chain blister agents. The longer chain blister agents, sesquimustard (Q) and bis[(2-chloroethylthio)-ethyl]ether (T) were present in all three samples along with a number of other related compounds that may provide synthetic procedure or source information [11].

The need for higher specificity and sensitivity has led to the application of element specific detectors such as flame photometric detection (FPD), thermionic detection (TID), atomic emission (AED) and electron capture detection (ECD). The simultaneous use of FID with one or more element specific detectors has also been demonstrated during dual or tri channel GC analysis using conventional and thermal desorption sample introduction. While data obtained with these detectors may provide strong collaborative evidence for the presence of chemical warfare agents, they cannot be used for full confirmation. Use of GC with one or more spectrometric technique such as MS is required to confirm the presence of chemical warfare agents.

Nerve and blister agents undergo hydrolysis in the environment [12] and methods are required under the Chemical Weapons Convention for retrospective detection and confirmation of these compounds. These compounds are significant as they would not be routinely detected in environmental samples and their identification strongly suggests the prior presence of chemical warfare agents. The degradation products of the chemical warfare agents, in particular the nerve agents, are non-volatile hydrolysis products that must be derivatized prior to GC analysis [13]. A variety of derivatization reagents, leading to the formation of pentafluorobenzyl, methyl, *tert*-butyldimethylsilyl and trimethylsilyl ethers (or esters), have been investigated to allow GC analysis of organophosphorus acids related to the nerve agents (e.g., alkyl methylphosphonic acids and methylphosphonic acid). Increasingly, liquid chromatography-electrospray-mass spectrometry (LC-ESI-MS), is being used for these types of analyses, as electrospray mass spectrometric data may be used to identify chemical warfare agents, their degradation products and related compounds in aqueous samples or extracts without the need for additional sample handling and derivatization steps [14].

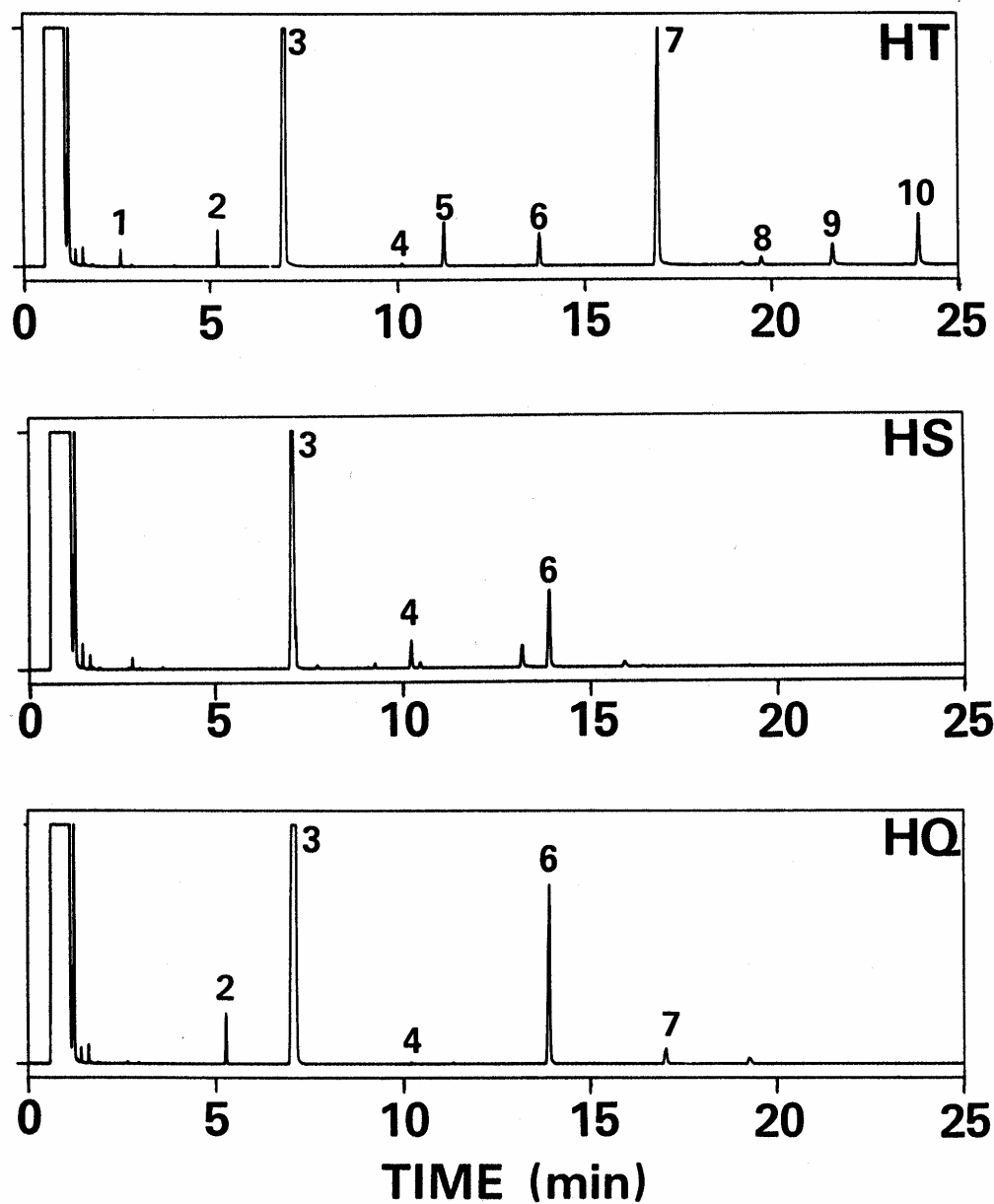


Figure 2. Capillary column GC-FID chromatograms of three munitions-grade mustard samples; HT (top), HS (middle) and HQ (bottom). Identified compounds include: 1. 1,4-thioxane, 2. 1,4-dithiane, 3. mustard (H), 4. bis(2-chloroethyl)disulfide, 5. 2-chloroethyl (2-chloroethoxy)ethyl sulfide, 6. sesquimustard (Q), 7. bis(2-chloroethylthioethyl)ether (T), 8. 1,14-dichloro-3,9-dithia-6,12-dioxatetradecane, 9. 1,14-dichloro-3,6,12-trithia-9-oxatetradecane and 10. 1,16-dichloro-3,9,15-trithia-6,12-dioxaheptadecane. (GC conditions: 15 m x 0.32 mm ID J&W DB-1; 50°C (2 min) 10°C/min 280°C (5 min)). Analysis performed at DRDC Suffield.

Mass spectrometry

Mass spectrometry [8, 9, 10, 14] is the method of choice for the detection and characterization of chemical warfare agents, their precursors, degradation products and related compounds. Extensive use has been made of GC-MS and the mass spectra of numerous chemical warfare agents and related compounds have been published, with the most common chemical warfare agent mass spectra being available in the OPCW, commercial or defence community databases.

The majority of MS data have been obtained under electron impact (EI) ionization conditions. However many of the chemical warfare agents, in particular the organophosphorus nerve agents and the longer chain blister agents related to mustard, do not provide molecular ion information under EI-MS. This hinders confirmation of these chemical warfare agents and makes identification of novel chemical warfare agents or related impurities difficult. For this reason, considerable effort has been devoted to the use of chemical ionization (CI) as a complementary ionization technique. This milder form of ionization generally affords molecular ion information for the chemical warfare agents and has been used extensively for the identification of related compounds or impurities in chemical warfare agent munition samples and environmental sample extracts. The characterization of these related compounds remains important during OPCW or other analyses since this data may provide an indication of the origin of the sample, the synthetic process utilized or the degree of sample degradation (weathering).

Methane, isobutane and ethylene gases were initially demonstrated as suitable CI gases for the acquisition of organophosphorus nerve agent molecular ion information [15]. More recently, the efficacy of ammonia CI-MS for organophosphorus nerve agents and related compounds was demonstrated and many laboratories now employ this complementary confirmation technique [16, 17]. Ammonia CI not only offers abundant molecular ion data but also affords a high degree of specificity as less basic sample components are not ionized by the ammonium ion. Additional structural data may be obtained through the use of deuterated ammonia CI, as this technique provides hydrogen/deuterium exchange data that indicates the presence of exchangeable hydrogen(s) in CI fragmentation ions. Finally, for full confirmation, the acquired EI and CI mass spectrometric data should be compared to authentic reference data obtained under identical experimental conditions.

Capillary column GC-MS/MS offers the analyst the potential for highly specific, sensitive detection of chemical warfare agents as this technique significantly reduces the chemical noise associated with complex biological or environmental sample extracts [18]. The specificity of product scanning with moderate sector resolution, as well as the specificity of ammonia CI, were demonstrated with a hybrid tandem mass spectrometer during analysis of painted panel samples circulated during an international round robin verification exercise.

The painted panel extract was contaminated with numerous hydrocarbons and only two of the three longer chain blister agents, sesquimustard (Q) and bis(2-chloroethylthioethyl)ether (T), could be identified during capillary column GC-MS (EI) analysis (Figure 3a). The arrow indicates the chromatographic retention time of the third blister agent, 2-chloroethyl (2-chloroethoxy)ethyl sulfide (O). The specificity of ammonia CI (Figure 3b) was clearly

demonstrated during this analysis. All three longer chain blister agents were identified in the presence of high levels of interfering hydrocarbons, as the hydrocarbons were not sufficiently basic to ionize. Similarly, it was possible to use the resolution of hybrid tandem mass spectrometry to discriminate between ions at m/z 123 arising from the longer chain blister agents from those ions at m/z 123 arising from the hydrocarbon background. The resultant GC-MS/MS chromatogram (Figure 3c), where only m/z 123 ions due to the blister agents were transmitted into the collisional activated dissociation cell of the MS, was virtually free of chemical noise and all three components were detected. The three longer chain blister agents were well resolved with the J&W DB-1701 capillary column, with all three components exhibiting similar product spectra during GC-MS/MS analysis [19].

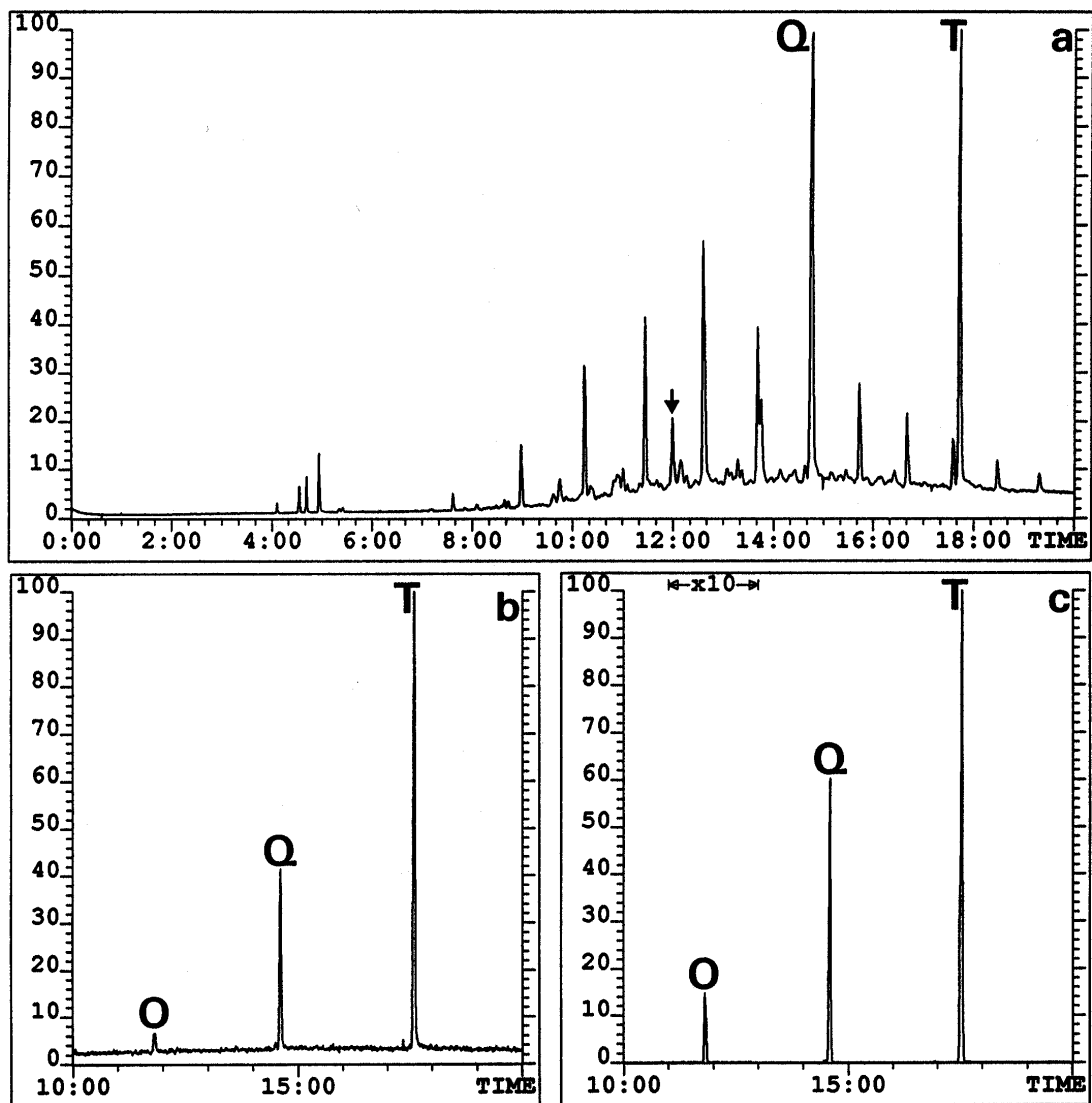


Figure 3. Capillary column a) GC-MS (EI), b) GC-MS (ammonia CI) and c) GC-MS/MS (EI) chromatograms obtained during analysis of international round robin painted panel extracts. Sequimustard (Q) and bis(2-chloroethylthioethyl)ether (T) were detected during EI analysis. The downward arrow in a) indicates the retention time of 2-chloroethyl (2-chloroethoxy)ethyl sulfide (O). This compound was masked by the sample matrix during EI analysis and was only detected following b) ammonia CI and c) MS/MS analysis. (GC conditions: 15 m x 0.32 mm ID J&W DB-1701, 40°C (2 min) 10°C/min 280°C (5 min), X-axis: time (minutes)). Analysis performed at DRDC Suffield.

Nerve and blister agents undergo hydrolysis in the environment and methods are required for retrospective detection and confirmation of these hydrolysis products. Hydrolysis products are significant as they are generally compounds that would not be routinely detected in environmental samples and their presence strongly suggest the prior presence of chemical warfare agents. The degradation products of the chemical warfare agents, in particular the nerve agents, are non-volatile hydrolysis products that must be derivatized prior to GC analysis. Alternatively aqueous samples or extracts may be analyzed by LC-MS, negating the need for additional sample handling steps and derivatization.

Thermospray mass spectrometry and, more recently, the atmospheric pressure ionization (e.g., ESI, ionspray and atmospheric pressure CI) techniques have enabled the direct mass spectrometric analysis of the hydrolysis products of chemical warfare agents [10]. These techniques may be interfaced to liquid chromatography for component separation, with thermospray having been largely superseded by atmospheric pressure ionization (API) for most LC-MS applications. LC-ESI-MS methods have been used for the direct analysis of chemical warfare agent hydrolysis products in a number of studies and have recently been used for the analysis of nerve agents. These new methods complement existing GC-MS methods for the analysis of chemical warfare agents and their hydrolysis products and LC-ESI-MS methods will replace some GC-MS methods used for the analysis of contaminated aqueous samples or extracts.

Mustard and longer chain blister agents hydrolyze to their corresponding diols, with thiodiglycol being the product formed following hydrolysis of mustard. Figure 4a illustrates a typical LC-ESI-MS chromatogram obtained for the aqueous extract of a soil sample taken from a former mustard storage site. The soil sample extract contained thiodiglycol (Figure 4b) and 6-oxa-3,9-dithia-1,11-undecanediol (Figure 4c), the hydrolysis products of blister agents mustard and bis(2-chloroethylthioethyl)ether, respectively. ESI-MS data for both compounds contained protonated molecular ions that could be used to confirm molecular mass and characteristic lower mass product ions [20].

Figure 5 illustrates the LC-ESI-MS chromatogram for a complex munitions-grade tabun sample. Tabun and a number of related compounds were identified based on their acquired ESI-MS data. The mass spectra contained $(M+H)^+$, $(M+H+ACN)^+$ ions and/or protonated dimers that could be used to confirm the molecular mass of each compound. Structural information was provided by inducing product ion formation in either the ESI interface or the quadrupole collisional cell of a MS/MS instrument. Product ions due to alkene loss from the alkoxy substituents, and the acetonitrile (ACN) adduct associated with these product ions, were generally observed. Figure 6 illustrates typical ESI-MS data obtained for tabun and three other nerve agents [21].

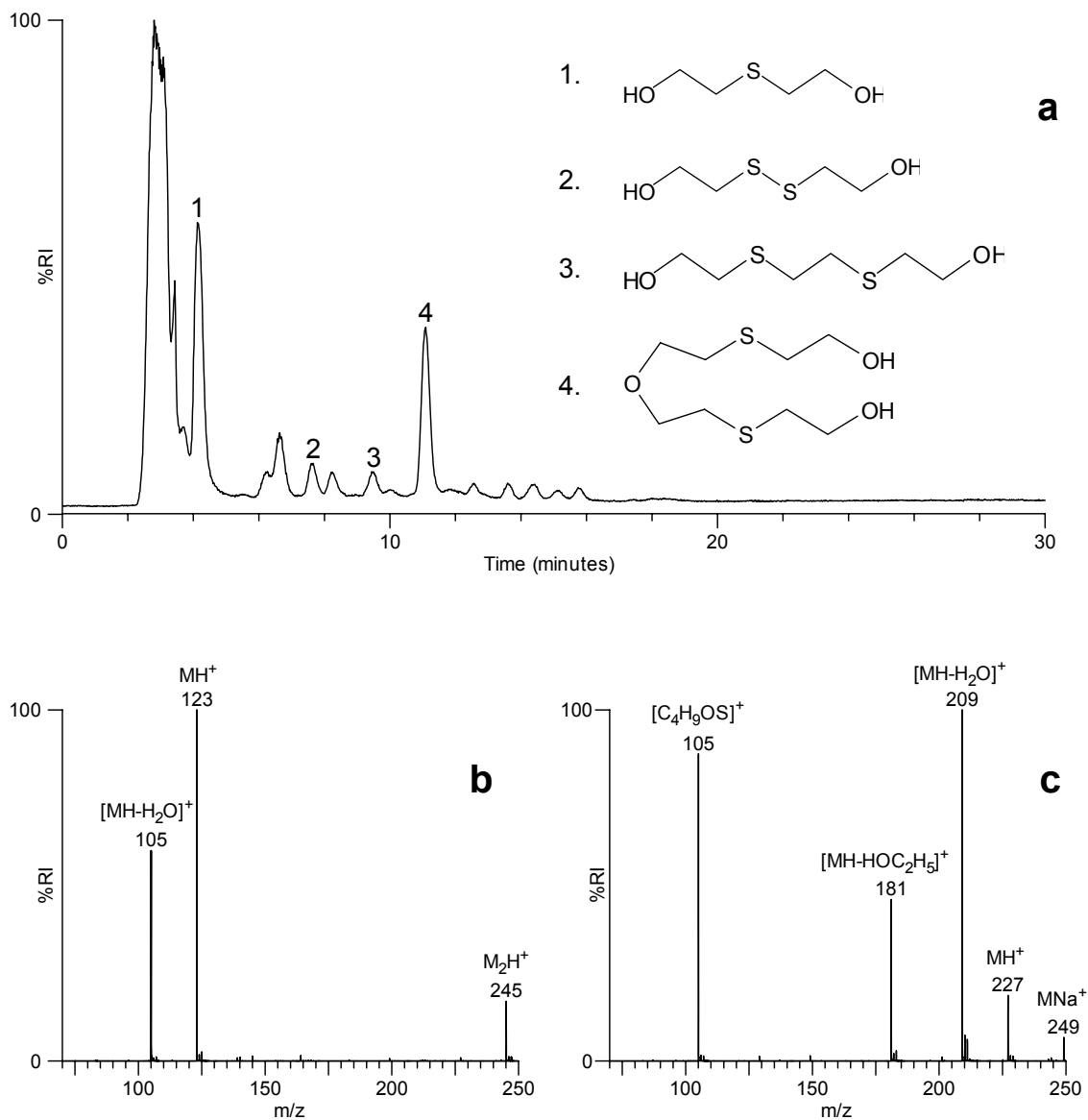


Figure 4. a) Packed capillary LC-ESI-MS chromatogram obtained for the water extract of a soil sample obtained from a former mustard site. ESI-MS data obtained for b) thiodiglycol (sampling cone voltage: 20 V) and c) 6-oxa-3,9-dithia-1,11-undecanediol (sampling cone voltage: 30 V). (LC conditions: 150 mm x 0.32 mm i.d. C_{18} , acetonitrile/water gradient). Analysis performed at DRDC Suffield.

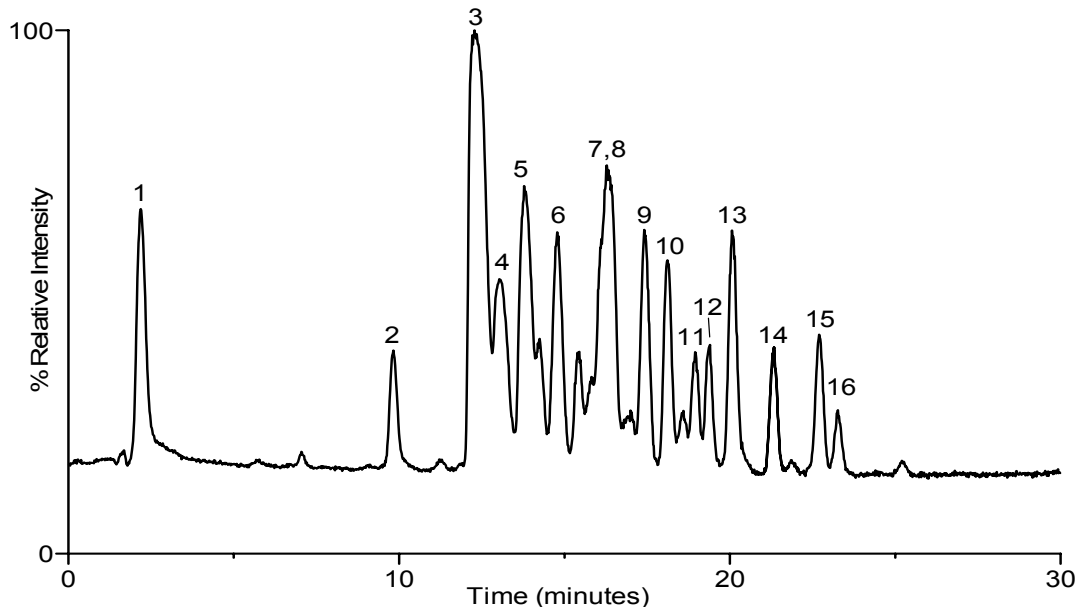


Figure 5. Packed capillary LC-ESI-MS chromatogram obtained for 0.1 mg/mL munitions-grade tabun sample. Tabun (peak number 3) and fifteen related organophosphorus compounds were identified by ESI-MS. (LC conditions: 150 mm x 0.32 mm i.d. C_{18} , acetonitrile/water gradient). Analysis performed at DRDC Suffield.

Considerable effort has been expended on the development of field portable MS and GC-MS instruments [22], as this technique holds the greatest promise for the confirmation of chemical warfare agents under field situations. The OPCW has available field portable GC-MS instrumentation that may be taken on-site to confirm the presence of chemical warfare agents. An atmospheric pressure MS/MS has also been developed and evaluated for real-time detection of nerve agents in air. Alternatively, air samples may be collected on Solid Phase Microextraction (SPME) fibres or on Tenax tubes that may be thermally desorbed into an on-site GC-MS instrument. Secondary ion mass spectrometry has been used for the detection of chemical warfare agents and their hydrolysis products on leaves, soil and concrete, offering a new option for the detection of these compounds on adsorptive surfaces. Finally, rapid separation and detection of chemical warfare agents has recently been demonstrated with ESI-ion mobility spectrometry (IMS)-MS. IMS is commonly employed in military devices (e.g., Chemical Agent Monitor) for rapid field detection and this approach could lead to the development of instrumentation for the analysis of aqueous samples.

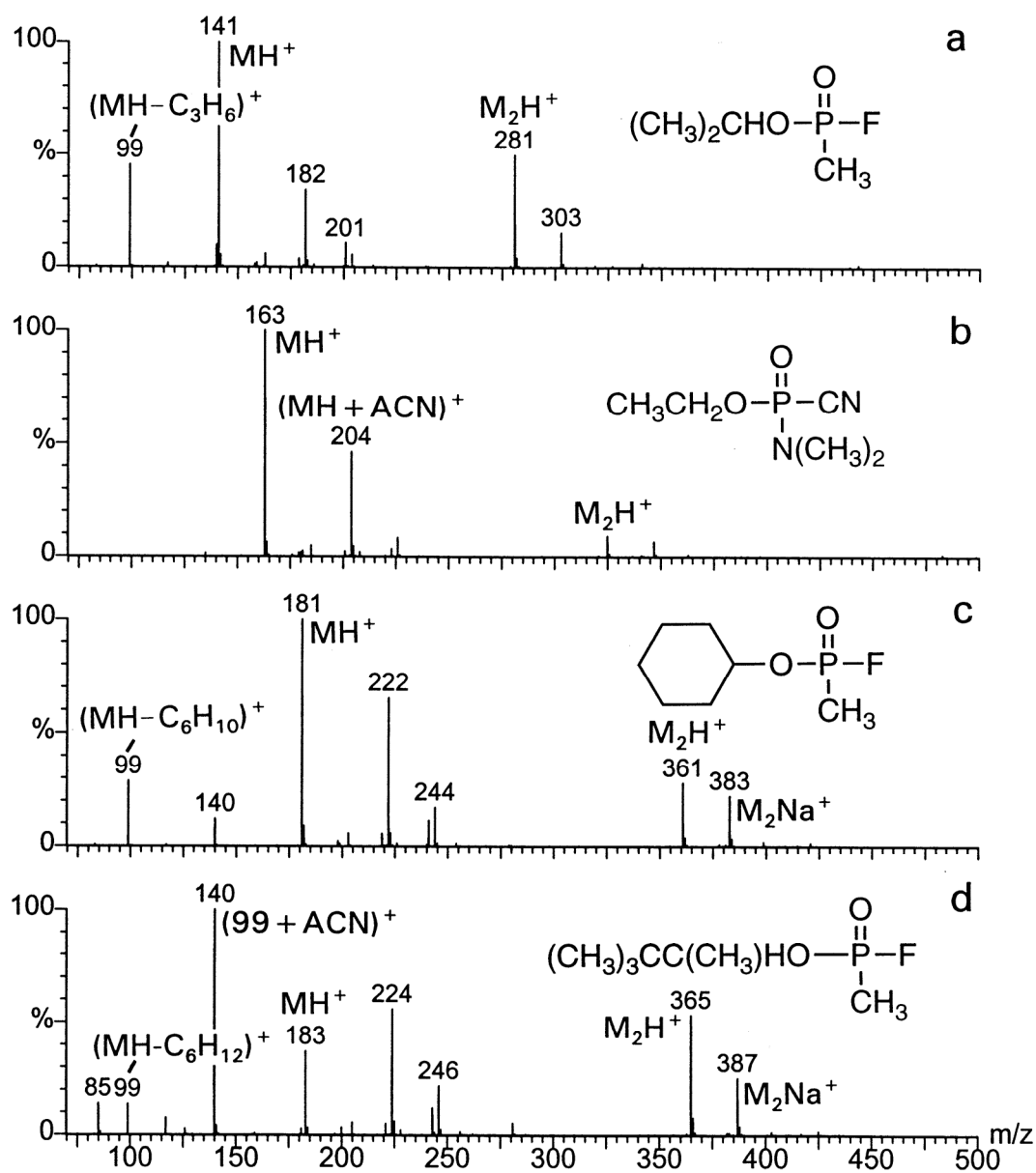


Figure 6. ESI-MS data obtained for a) sarin (GB), b) tabun (GA), c) cyclohexyl methylphosphonofluoridate (GF) and d) soman (GD) with a sampling cone voltage of 20 volts. Analysis performed at DRDC Suffield.

Other methods

NMR is an important technique for the structural analysis and characterization of chemical warfare agents [23], particularly for the authentication of reference materials or unknown chemical warfare agents and related compounds. The presence of heteronuclei such as ^{31}P and ^{19}F in the nerve agents leads to diagnostic splitting patterns and coupling constants due to ^1H - ^{31}P and ^1H - ^{19}F spin-spin coupling. The utility of NMR for analysis of complex sample mixtures or for trace analysis is somewhat limited. Specific heteronuclear experiments such as ^{31}P NMR may be used to identify organophosphorus nerve agents in complex matrices. Characteristic chemical shifts of compounds containing a phosphorus-carbon bond and splittings due to phosphorus-fluorine spin-spin coupling can be used to screen for the presence of nerve agents. However, ^{31}P chemical shifts are sensitive to temperature, concentration, and solvent and the identification must be supported with additional spectrometric data such as MS. Two-dimensional correlation experiments have been used to help in structural elucidation of unknowns in contaminated samples, making NMR a valuable technique to be used alongside other spectrometric techniques.

Condensed phase infrared (IR) data exists for many chemical warfare agents and related compounds as this technique was routinely used prior to the advent of GC-MS. Capillary column GC-FTIR offers considerably more promise for the identification and characterization of chemical warfare agents in multiple component sample extracts and has been utilized as a complementary confirmation technique [24]. Sensitivity is generally poorer than that obtained by mass spectrometry but may be improved by using large volume (e.g., 50 μL) injections with peak compression onto an uncoated pre-column with lightpipe technology or through the use of cryodeposition.

Safety and disposal

Chemical warfare agents are extremely hazardous and lethal compounds. They should only be used in designated laboratories by personnel trained in safe-handling and decontamination procedures and with immediate access to medical support. Safety and standard operating procedures must be developed and approved before any chemical warfare agents are handled. Chemical warfare agents should only be used in laboratory chemical hoods with a minimum face velocity of 150 linear feet per minute that are equipped with emission control devices that limit exhaust concentration to below 0.0001 mg/m^3 . Personnel handling chemical warfare agents should wear rubber gloves, lab coats, and full-faceshields and keep a respirator (gas mask) and therapeutic devices within easy reach. Sufficient decontaminant to destroy the chemical warfare agent being handled must be on hand before commencing operations.

Nerve and blister agents can be destroyed using saturated methanolic solutions of sodium or potassium hydroxide. Decontaminated chemical warfare agents must be disposed of in an environmentally approved method according to local legislation.

LC-MS of chemical warfare agents: A review

Background

The ending of the Cold War and the widespread acceptance of the Chemical Weapons Convention has reduced the likelihood of battlefield chemical weapons use, but there remains a serious concern world-wide that other parties may make use of chemical warfare agents against civilian or military targets. Analytical methods for chemical warfare agent identification will be required following an incident as sampling and analysis will be conducted to support treaty compliance, allegations of use and forensic investigations. Considerable research effort has been expended over the past several years due to increased security concerns and this review covers the recent advances and applications of liquid chromatography-mass spectrometry (LC-MS) for the detection, characterization and confirmation of chemical warfare agents and their degradation products. Potential areas for new research efforts will also be identified.

Chemical warfare agent containing samples typically contain multiple components that are best characterized following chromatographic separation. Gas chromatography has been used extensively for the separation and identification of chemical warfare agents, with gas chromatography-mass spectrometry (GC-MS) being used frequently for the characterization of these compounds [6-10]. GC-MS analysis methods form the cornerstone of the Technical Secretariat of The Organization for the Prohibition of Chemical Weapons (OPCW) recommended analytical procedures and have been used extensively during designated laboratory proficiency testing [25]. Electron impact mass spectrometric data and spectrometric or spectroscopic data from a second analytical technique (e.g., LC-MS, FTIR or NMR) have typically been acquired to meet OPCW identification requirements, as the OPCW demands that identified compounds must be confirmed by at least two different spectrometric or spectroscopic methods.

Nerve and blister agents undergo hydrolysis in the environment [12] and methods are required for the detection and confirmation of the hydrolysis products as well. These compounds are significant as they would not be routinely detected in environmental samples and their identification strongly suggests the prior presence of chemical warfare agents. Many degradation products of chemical warfare agents, especially those formed following hydrolysis of nerve agents, are much less volatile than the parent compounds and must be derivatized prior to GC analysis. A number of derivatization reagents, leading to the formation of pentfluorobenzyl, methyl, or silyl esters have been investigated to allow GC-MS analysis of hydrolysis products of chemical warfare agents [13]. The most commonly targeted degradation compounds include the alkyl methylphosphonic acids and methylphosphonic acid associated with nerve agent hydrolysis and the primary hydrolysis product of mustard, thiodiglycol.

Wils and Hulst were the first to demonstrate the use of LC-MS for the direct analysis of nerve agent hydrolysis products [26] and VX [27], using thermospray ionization, a technique that has now been superseded by atmospheric pressure ionization (API). Increasingly researchers

have developed API based LC-MS methods (e.g., electrospray (ESI), ionspray (IS) and atmospheric pressure chemical ionization (APCI)) as complementary or replacement methods for the characterization of chemical warfare agents and/or their degradation products. A number of LC-MS methods have been reported for the confirmation of these compounds, with this technique being used most frequently during the analysis of aqueous samples or extracts. Review papers on LC-MS analytical methods for chemicals warfare agents and related compounds have been published by both Black and Read [14] and Hooijschuur, Kientz and Brinkman [10], with the more recent review focusing on the chromatographic separation of chemical warfare agents over the 1996 to 2001 time period [10]. In a more targeted review, Noort, Benschop and Black [28] reviewed LC-MS and other methods dealing with biomonitoring of exposure to chemical warfare agents. In many cases LC-MS proved to be an attractive alternative to GC-MS for aqueous analyses, as both the organophosphorus chemical warfare agents and their hydrolysis products could be analysed directly without the need for additional sample handling and derivatization steps associated with GC-MS analysis [13].

LC-MS analyses

LC- MS has become an important method or complementary method for the identification of chemical warfare agents, their hydrolysis products and related compounds in a variety of different sample types [20, 21, 29-49]. It has been used most commonly for the analysis of aqueous samples, including biological fluids and aqueous extracts of sample media such as soil. Table 1 lists recently reported methods by sample media and includes the mode of ionization, LC conditions and compounds analysed.

The majority of the LC-MS applications listed in Table 2 involve the analysis of degradation products of chemical warfare agents as these compounds can be analysed directly using an API method of ionization. Both positive ion (PI) and negative ion (NI) modes have been used with advantages in selectivity [40] or sensitivity [37] generally being cited as the reasons for the choice. More universal screening of the wide range of possible degradation products associated with chemicals scheduled by the CWC would likely involve a PI screening procedure or one that targets a number of key compounds using both PI and NI modes depending on the compound [37]. Read and Black demonstrated this approach during the development of a LC-APCI-MS screening method that utilized both PI and NI mode for the determination of 19 acidic, neutral and basic CW agent degradation products in water [37].

Table 2. LC-MS analyses of chemicals related to the CWC.

Media	Ref	Ionization	Chromatography	Compounds Analysed
Water	29	ESI (PI)	- Mixed C ₈ /C ₁₈ (250 X 2.1 mm) column. - MeOH/water (0.1% formic acid) gradient at 200 µL/min.	- Alkyl methylphosphonic acids, alkyl ethylphosphonic acids, alkyl alkylphosphonic acids and dialkyl alkylphosphonates.
Water	30	ESI (PI)	- C ₁₈ (150 X 0.32 mm) column. - ACN/water (0.1% trifluoroacetic acid) gradient at 5 µL/min.	- Munitions grade mustard hydrolysis products including thiodiglycol and longer chain diols.
Water	31	APCI (PI)	- C ₁₈ (250 X 2.1 mm) column. - water (0.001 to 0.05 M ammonium acetate) isocratic at 250 µL/min.	- Hydrolysis products of VX, lewisite and nitrogen mustard using post column derivatization.
Water	32	ESI (PI)	- C ₁₈ (150 X 0.32 mm) column. - ACN/water (0.1% trifluoroacetic acid) gradient at 5 µL/min.	- VX and numerous VX degradation products and related compounds.
Water	33	ESI (PI)	- C ₁₈ (150 X 0.32 mm) column. - ACN/water (0.1% trifluoroacetic acid) gradient at 5 µL/min.	- Nerve agents, sarin, soman, tabun and cyclohexyl methylphosphonofluoridate.
Water	34	Fast atom bombardment (PI)	- C ₁₈ (150 X 1.5 mm) column. - ACN/water (0.005 M ammonium acetate) isocratic at 100 µL/min.	- Derivatized (<i>p</i> -bromophenacyl) alkyl phosphonic acids.
Water	35	IS (NI)	- PGC (150 X 2.1 mm) column. - ACN/water (trifluoroacetic acid) gradient/isocratic at 200 µL/min.	- Alkylphosphonic acids, alkyl methylphosphonic acids and alkyl ethylphosphonic acids.
Water	36	IS (NI)	- PGC (150 X 2.1 mm) column. - ACN/water (trifluoroacetic acid) gradient/isocratic at 200 µL/min.	-Alkylphosphonic acids,

Water	37	APCI (PI/NI)	- C ₁₈ (250 X 2.0 mm) column. - MeOH/water (0.02M ammonium formate) gradient at 200 µL/min.	- Hydrolysis products of ten nerve agents, mustard, nitrogen mustard and quinuclidinyl benzilate (BZ)
Water	38	ESI (PI)	- C ₁₈ (150 X 0.32 mm) column. - MeOH/water (0.2% formic acid) isocratic at 6 µL/min.	-Thiodiglycol and other hydrolysis products of sulfur mustards.
Water	21	ESI (PI)	- C ₁₈ (150 X 0.32 mm) column. - ACN/water (0.1% trifluoroacetic acid) gradient at 16 µL/min.	Nerve agents, sarin, soman, tabun and cyclohexyl methylphosphonofluoridate and their hydrolysis products.
Water	39	ESI (PI)	- C ₁₈ (150 X 0.32 mm) column. - ACN/water (0.1% trifluoroacetic acid) gradient at 16 µL/min.	- Sarin and its degradation products and numerous related compounds.
Water	40	ESI (NI)	- C ₁₈ (150 X 2.1 mm) column. - MeOH/water (0.01M ammonium formate) gradient at 200 µL/min.	- Alkyl methylphosphonic acids.
Soil	38	ESI (PI)	- C ₁₈ (150 X 0.32 mm) column. - MeOH/water (0.2% formic acid) isocratic at 6 µL/min.	-Thiodiglycol and other hydrolysis products of sulfur mustards.
Soil	21, 41	ESI (PI)	- C ₁₈ (150 X 0.32 mm) column. - ACN/water (0.1% trifluoroacetic acid) gradient at 16 µL/min.	Nerve agents, sarin and soman and their hydrolysis products.
Soil	40	ESI (NI)	- C ₁₈ (150 X 2.1 mm) column. - MeOH/water (0.01M ammonium formate) gradient at 200 µL/min.	- Alkyl methylphosphonic acids.
Soil	20,42	ESI (PI)	- C ₁₈ (150 X 0.32 mm) column. - ACN/water (0.1% trifluoroacetic acid) gradient at 10 µL/min.	- Thiodiglycol and longer chain diols associated with hydrolysis of munitions grade mustard.
Munition	43	APCI (PI)	- C ₁₈ (100 X 2.1 mm) column. - ACN/water (0.05M ammonium acetate) gradient at 250 µL/min.	- Phosphorothioates and related compounds.

Munition	21	ESI (PI)	- C ₁₈ (150 X 0.32 mm) column. - ACN/water (0.1% trifluoroacetic acid) gradient at 16 µL/min.	- Tabun, its hydrolysis product and numerous related compounds.
Synthetic	42	ESI (PI)	- C ₁₈ (150 X 0.32 mm) column. - ACN/water (0.1% trifluoroacetic acid) gradient at 10 µL/min.	- Tabun and numerous tabun related compounds
Synthetic	44	ESI (PI)	- C ₁₈ (250 X 2.0 mm) column. - MeOH/water (0.02M ammonium formate) gradient at 200 µL/min.	- Hydrolysis and oxidation products of two longer chain sulfur vesicants (Q and T).
Urine	45	ESI (PI)	- C ₁₈ (250 X 2.0 mm) column. - MeOH/water (0.02M ammonium formate) gradient at 200 µL/min.	-Beta-lyase metabolites of sulfur mustard.
Urine	46	ESI (PI/NI)	- C ₁₈ (150 X 2.0 mm) column. - ACN/water (0.05% formic acid) gradient at 200 µL/min.	- Sulfur mustard metabolite 1,1'-sulfonylbis[2-S-(N-acetylcysteinyl)ethane].
Serum	47	ESI (PI/NI)	- PRP-X100 (200 X 0.32 mm) column. - ACN/water (0.5% formic acid) isocratic at 20 µL/min.	-Isopropyl methylphosphonic acid.
Serum	34	Fast atom bombardment (PI)	- C ₁₈ (150 X 1.5 mm) column. - ACN/water (0.005 M ammonium acetate) isocratic at 100 µL/min.	- Derivatized (<i>p</i> -bromophenacyl) alkyl phosphonic acids.
Serum	48	ESI (PI)	- C ₁₈ (150 X 0.30 mm) column. - ACN/water (0.2% formic acid) gradient at 6 µL/min.	- Albumin/sulfur mustard adducts
Plasma	49	APCI (PI)	- OD-H (250 X 4.6 mm) column. - Hexane/isopropanol isocratic at 800 µL/min.	- Enantiomers of VX

APCI, IS and ESI have all been utilized for the analysis of chemical warfare agents and their degradation products, with ESI being preferred for the lower flow rates associated with packed capillary LC separation [20, 21, 38]. APCI and IS methods have usually been associated with the use of larger bore LC columns and higher flow rates (e.g., 200 $\mu\text{L}/\text{min}$) and were found to be less susceptible to variable adduct ion formation than ESI [37]. However, regardless of the API technique or instrument used, the acquired mass spectra remain similar in ion content, exhibiting adduct ions (e.g., $[\text{M}+\text{H}]^+$ or $[\text{M}+\text{Na}]^+$) that may be used to determine molecular mass and characteristic product ions (e.g., $[\text{M}+\text{H}-\text{H}_2\text{O}]^+$ or $[\text{M}+\text{H}-\text{C}_n\text{H}_{2n}]^+$) indicative of the compound's structure. Relative intensities of the characteristic ions will vary depending on instrumental conditions [21].

Many recent publications have focused on the direct analysis of hydrolysis products related to the more common chemical warfare agents, including, thiodiglycol and longer chain diols that form following hydrolysis of mustard and munitions grade mustard formulations [20, 30, 37, 38, 42, 44] and alkyl methylphosphonic acids and methyl phosphonic acid that form following hydrolysis of the nerve agents [21, 29, 31, 32, 35-37, 39-41, 47]. Additional degradation products related to nitrogen mustard, quinuclidinyl benzilate and less common nerve agents included in the CWC schedules have been included in several reports, often associated with preparing for or actual OPCW proficiency testing [25, 29, 35, 37]. Derivatization was employed in several instances to enhance sensitivity [31, 34], but for the most part derivatization has only been used to facilitate GC-MS analyses [13].

An important advantage of LC-ESI-MS is that it may also be used for the identification of intact organophosphorus chemical warfare agents and related compounds that are often present in samples or sample extracts due to degradation or synthetic procedure [21, 32, 33, 39, 41, 42, 49]. Identification and characterization of these related sample components remains an area of interest as the identification of these compounds may provide source or synthetic clues during an investigation. However it should be noted that the CW agent, mustard, does not ionize during LC-ESI-MS and its determination in samples should be done by GC-MS [42] or by another spectrometric or spectroscopic technique.

LC separations are usually performed on C_{18} LC columns with acetonitrile (ACN) or methanol (MeOH)/water gradients using trifluoroacetic acid, formic acid or ammonium formate modifiers. Trifluoroacetic acid generally provides the best chromatographic resolution [37] and this modifier has been used frequently for lower flow rate analyses [20, 21, 39]. Trifluoroacetic acid will suppress analyte signal at higher flow rates and may not be the best choice for NI work as it could compete with the analyte during API-MS. Ammonium formate was selected by Black and Read [37] as a buffer comprise for a broad screening procedure where both PI and NI data were acquired. Gradient separations with C_{18} provided the flexibility to analyse a variety of analytes from small, polar hydrolysis products, such as thiodiglycol and methylphosphonic acid, to larger, less polar compounds such as VX and related compounds [32]. The major problem associated with use of C_{18} columns remains the poor retention for the smaller, polar hydrolysis products. Improvements have been observed with the use of porous graphitic carbon (PGC) or other columns [35, 36].

Chiral separations can be quite valuable for toxicological studies or during the development of antidotal therapies. Smith reported the first chiral separation of the two enantiomers of VX using a Chiralcel OD-H column and a hexane/isopropanol mobile phase. Both enantiomers were completely resolved during the isocratic LC separation [49].

Detection limits

Instrumental improvements have resulted in LC-MS detection limits that approach those reported during GC-MS analyses. Newer instruments have made it routinely possible to detect compounds in full scanning mode in the 0.5 to 5 ng range and at levels about two orders of magnitude better during selected ion monitoring (SIM). Reported detection limits for the determination of chemical warfare agents hydrolysis products using LC-API-MS have been found to be quite compound dependent. In an earlier paper, Black and Read used SIM and detected neutral and basic compounds in the < 200 pg range (or < 10 ng/mL water), but some acidic compounds, like methylphosphonic acid and thiodiglycol, exhibited detection limits of up to 8 ng (or 400 ng/mL) [29]. Later improvements to the above method, including the use of both PI and NI, dropped detection limits by a factor of four at the higher end [37]. A similar method, using LC-ESI-MS (NI), resulted in SIM detection limits that ranged from 250 pg to 5 ng, with methylphosphonic acid being at the upper limit [40].

LC-ESI-MS detection limits for triethyl phosphate, a compound resistant to hydrolysis but similar to chemical warfare agents were determined by D'Agostino et al. This compound could be detected at 50 pg under full scanning conditions [21]. Detection limits may be improved by employing larger volume injections with peak compression. Hooijschuur et al. reported full scanning detection limits of 500 to 800 ng/mL with this technique for longer chain diols associated with mustard hydrolysis. Finally some of the best absolute detection limits were reported during LC-ESI-MS/MS in the multiple reaction monitoring (MRM) mode. Noort et al. reported an absolute detection limit of 2 pg for isopropyl methylphosphonic acid [47] and 4 pg for a mustard adduct [48].

Structural elucidation

API-MS and API-MS/MS have been used for a number of structural elucidation studies, frequently without the need for LC separation. The OPCW requires specific identification of P-alkyl substituents and to this end van Baar, Hulst and Wils were able to differentiate iso- and n-propylphosphonic acids using tandem mass spectrometry [50]. This method was extended by Cooper et al. to include numerous dialkyl propylphosphonates and alkyl propylphosphonochloridates [51].

D'Agostino, Hancock and Provost demonstrated the applicability of in-source fragmentation for identification purposes during LC-ESI-MS analysis of a complex sample of degraded VX [32], as well as for other samples [21, 30, 33, 39, 42]. Doubly charged ions, observed for bis[2-(diisopropylamino)ethyl] sulfide and other longer chain bis(diisopropylamino)thioalkanes, at lower sampling cone voltages were completely resolved

with moderate resolution and could be easily assigned based on the half mass spacing in the $[M+2H]^{2+}$ isotopic cluster. Higher sampling cone voltages resulted in the production of numerous characteristic product ions that were used to help identify more than 25 VX related compounds [32]. Bell et al. investigated similar compounds and detailed extensively the reactions and fragmentation pathways of two isomeric O-alkyl S-(2-dialkylamino)ethyl methylphosphonothiolates using an ion trap equipped with an ESI source [52]. Interestingly, they were able to produce a number of product ions from the $[M+Na]^+$ ion of a VX related pyrophosphate using this method. Additional ESI studies have also been performed on isotopically labeled dimethyl methylphosphonate ions [53] and *N,N*-dialkylaminoethanols [54].

Acquiring higher resolution data for chemical warfare agents and related compounds, important for the identification of previously uncharacterized compounds, was greatly aided by the introduction of instruments with time-of-flight (TOF) mass analysers. These instruments may be used to acquire full scanning higher resolution data (typically 5000 to 17000 resolution, 50% valley) for sample components without the signal loss associated with magnetic sector instrumentation. D'Agostino et al. demonstrated the utility of high resolution LC-ESI-MS and LC-ESI-MS/MS data for the identification of sarin related compounds in snow [39], during the identification of numerous tabun impurities in a synthetic sample [42], and for the determination of longer chain diols in soil samples collected from a former mustard storage site [20]. Errors associated with the mass measurements during these analyses were generally < 0.001 Da. Liu et al. also recently demonstrated the use of high resolution LC-ESI-MS in NI mode for the confirmation of spiked alkyl methylphosphonic acids in water and soil samples [40].

Related investigations

Capillary electrophoresis (CE) was used as the means of separation during the first analysis of chemical warfare agent degradation products using API-MS [55]. This means of separation is generally not as robust or as easy to interface to API-MS instruments as LC and has not been used as frequently as LC for the separation of chemical warfare agents and related compounds. Nasser et al. used CE with indirect UV for trace determinations in soil and water [56], while Mercier et al. investigated CE-MS for the determination of phosphonic acids in aqueous samples on several occasions [35, 36, 57].

Ion mobility spectrometry (IMS), a technology used in hand-held military detectors for chemical warfare agents, has shown promise for very rapid separation of chemical warfare agent degradation products [58] and simulants [59] in an electrospray ionization atmospheric pressure ion mobility orthogonal reflectron time-of-flight mass spectrometer. Sodiated and protonated adducts were obtained for a number of phosphonic acids, thiodiglycol, and 1,4-dithiane [58]. The observance of ESI-MS data for 1,4-dithiane dissolved in water/methanol (5% acetic acid) was unusual, as other researchers have been unsuccessful in producing ESI-MS data from relatively non-polar compounds such as mustard, 1,4-oxathiane, and 1,4-dithiane [42].

Smith and Shih [60] compared ESI and APCI data obtained for common chemical warfare agent hydrolysis products to that obtained by particle beam MS using flow injection analysis. Most of the compounds investigated did not produce a molecular ion, but the particle beam MS data did contain sufficient fragmentation ions to identify each of the target compounds.

API-MS/MS using flow injection analysis has been applied in biomonitoring applications [28, 61] where chromatography was not required for identification. Similarly, target compounds in proficiency testing samples, could be characterized using ESI-MS/MS without the need for chromatographic separation [25], although analysts must be aware of the potential for ion suppression by more dominant sample components.

The CWC also includes in its schedules candidate toxins that were reviewed in the past [14] but were not reviewed at this time. This would be better treated as a separate subject given the explosive growth in biological and proteomic applications of mass spectrometry. Finally, LC-MS methods for toxic industrial chemicals, including pesticides [62], which might be used in a terrorist scenario or as agents of expediency, were also not included in this review.

Future areas for research

A number of possible areas of future study were identified. To date, most of the focus on LC-API-MS applications for chemical warfare agents has focused on environmental sample such as soil or water. These types of samples would be significant for a battlefield scenario but may not be as relevant following a terrorist event. The rapid analysis of biological samples will be extremely important in this situation from both a forensic (prosecution) perspective and to determine exposure within a population. Read and Black [45, 46] and Noort et al. [48] have recently reported specific, sensitive LC-MS methods that could be used. PI and NI ESI-MS data were obtained by Read and Black for 1,1'-sulfonylbis[2-S-(N-acetylcysteinyl)ethane, a mustard metabolite that was detected in human urine following exposure. An isotope dilution GC-MS/MS method has also been developed at the Center for Disease Control which could be applied to the detection and identification of chemical warfare agent degradation products [63]. In general, the difficulties associated with complex biological fluids and tissues remain a concern.

Forensic media collected at the scene of a terrorist attack could well involve the collection of samples from within an enclosed space, such as an office building. This has been an area of interest within D'Agostino's group, which has collaborated with the Royal Canadian Mounted Police in a study investigating media that might be collected during a forensic investigation involving the use of chemical warfare agents. A variety of sample media, including flooring, wall surfaces, office fabrics, window coverings and paper products or packaging, have been considered for investigation. Chemical warfare agents were spiked onto these media, recovered and positively identified in all cases. In some cases LC-ESI-MS/MS analysis was preferred to reduce chemical interference [64]. Other potential terrorist scenarios should be identified with a focus on potential sampling media and appropriate means of identification.

Improvements could also be made in the chromatographic resolution of the lower molecular mass, more polar hydrolysis products of chemical warfare agents, as they are generally poorly retained during most analyses. Matrix problems and ion suppression have also been indicated in some papers and noted during the analysis of aqueous samples from a military site, but this issue has not been addressed.

Detection limit improvements could be achieved by using narrower bore columns operating with flows in the nanolitre/minute range. Separation times could also be reduced with the use of new higher pressure LC systems that use LC columns with smaller particle sizes (e.g., Ultra Performance LC). Improvements in sensitivity and speed of analysis might also be achieved using IMS or high field asymmetric waveform ion mobility spectrometry (FAIMS) mass spectrometry [65], approaches that have the potential to minimize separation times.

D'Agostino has created an ESI-MS library containing data for about 60 chemical warfare agents, hydrolysis products and related compounds which is available on the Internet [66]. It contains both higher and lower sampling voltage mass spectra with the former containing more product ion information. During most ESI-MS analyses, the molecular mass will be evident, simplifying identification and limiting the number of possible matches in the mass spectral database. While ESI-MS data is not as amenable to database searching as EI-MS data, spectra obtained with different instruments generally exhibit the same ions, albeit with differences in their relative intensities. Fits may not be as good as EI-MS, but use and creation of API-MS databases will aid future analyses, particularly in cases where standards are unavailable.

LC-API-MS has not been used in a field portable role like GC-MS, but the versatile nature of this approach has researchers interested in developing field portable instrumentation [67]. A number of research efforts, including the development of a field portable chemical warfare agent analysis platform at DRDC Suffield for the Canadian NBC Company, are presently underway. It would be advantageous to utilize instrumentation based on API-MS since this technique has the potential to rapidly detect and identify chemical warfare agents and their degradation products as well as selected toxic industrial chemical, toxins and biological warfare agent biomarkers.

DRDC Suffield LC-ESI-MS methods

DRDC Suffield has been active in the development and application of LC-ESI-MS for the identification of chemical warfare agents, their hydrolysis products and related compounds since the late 1990's, publishing the following papers dealing with the subject area:

1. D'Agostino, P.A., Provost, L.R. and Hancock, J.R. (1998). Analysis of mustard hydrolysis products by packed capillary liquid chromatography-electrospray mass spectrometry. *J. Chromatogr. A*, 808, 177-184.
2. D'Agostino, P.A., Hancock, J.R. and Provost, L.R. (1999). Analysis of o-ethyl s-[2-(diisopropylamino)ethyl] methylphosphonothiolate (VX) and its degradation products by packed capillary liquid chromatography-electrospray mass spectrometry. *J. Chromatogr. A*, 837, 93-105.
3. D'Agostino, P.A., Hancock, J.R. and Provost, L.R. (1999). Packed capillary liquid chromatography-electrospray mass spectrometry analysis of organophosphorus chemical warfare agents. *J. Chromatogr. A*, 840, 289-294.
4. D'Agostino, P.A., Hancock, J.R. and Provost, L.R. (2001). Determination of sarin, soman and their hydrolysis products in soil by packed capillary liquid chromatography-electrospray mass spectrometry. *J. Chromatogr. A*, 912, 291-299.
5. D'Agostino, P.A., Hancock, J.R. and Provost, L.R. (2001). Electrospray mass spectrometry of chemical warfare agents. *Advances in Mass Spectrometry*, 15, 297-316.
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7. D'Agostino, P.A., Hancock, J.R. and Chenier, C.L. (2003). Mass spectrometric analysis of chemical warfare agents and their degradation products in soil and synthetic samples. *Eur. J. Mass Spectrom.*, 9, 609-618.
8. D'Agostino, P.A., Hancock, J.R. and Chenier, C.L. (2004). Packed capillary liquid chromatography-electrospray ionization (tandem) mass spectrometry of mustard hydrolysis products in soil. *J. Chromatogr. A*, 1058, 97-105.

The methods have focused largely on the development and application of aqueous extraction for sample preparation and LC-ESI-MS and LC-ESI-MS/MS for identification purposes. A variety of sample types containing chemical warfare agents have been investigated including water, snow, soil, munitions and synthetic samples. Typically, a 1 g to 2 g portion of a sample (e.g., soil) suspected to contain chemical warfare agents was weighed and placed in a 20 mL (or similar) screw capped glass scintillation vial. A volume of water, sufficient to completely immerse the sample was added (e.g., 4 mL) and the sample was subjected to ultrasonic vibration for 10 min. A portion of the extract (e.g., 1 mL) was removed and centrifuged at

14,000 rpm to remove any fines. The upper portion of the centrifuged sample (e.g., 0.75 mL) was placed in a 1.8 mL glass autosampler vial for LC-ESI-MS or LC-ESI-MS/MS analysis. Aqueous samples were simply centrifuged in a similar manner to reduce the possibility of fines introduction.

DRDC Suffield has a Waters QTOF Ultima tandem mass spectrometer equipped with a Z-spray electrospray interface. LC-ESI-MS and LC-ESI-MS/MS data were typically acquired with an electrospray capillary voltage in the 1 kV to 3 kV range and a sampling cone voltage of 35 V. The collision energy was generally maintained at 5 V for LC-ESI-MS operation and was varied from 2 V to 15 V (depending on the precursor ion selected) for LC-ESI-MS/MS operation. Argon was continually flowing into the collision cell at 9 psi during both LC-ESI-MS and LC-ESI-MS/MS operation. Nitrogen desolvation gas was introduced into the interface (80°C) at a flow rate of 300 L/h and nitrogen cone gas was introduced at a flow rate of 50 L/h. ESI-MS or ESI-MS/MS data were generally acquired from 70 to 700 Da (1 s with a 0.1 s interscan delay). High resolution ESI-MS and ESI-MS/MS were used to identify all target compounds and elucidate structural information that aided in the identification of unknowns. Data were typically acquired in the continuum mode with a resolution of 9000 (V-mode, 50% valley definition).

Chromatographic separations were typically performed with a Waters CapLC using a 5% to 75%B gradient over 30 minutes and a flow rate of 10 µL/min. The following solvent compositions were prepared for the mobile phase: Solvent A (0.1% trifluoroacetic acid in water) and Solvent B (acetonitrile). LC separations were performed with a MicroTech 150 mm x 0.32 mm i.d. fused-silica capillary columns packed with Zorbax C18 SB (5 µm particle size). An autosampler was used to introduce 1 µL samples of the aqueous extracts.

Specific experimental details may be obtained from the listed papers in the experimental sections.

The papers listed highlight the potential of LC-ESI-MS for the direct determination of organophosphorus chemical warfare agents and their principal hydrolysis products in aqueous samples or extracts during a single analysis without the need for derivatization. It should be noted that mustard and longer chain organosulfur vesicants did not ionize well in the ESI interface and analysis of these chemical warfare agent should be performed by GC-MS. However the hydrolysis products of mustard and longer chain organosulfur vesicants did ionize in the ESI-interface and these compounds may be determined using LC-ESI-MS.

Recent investigations have focused on additional sample media that might be collected during forensic investigations of an indoor office environment suspected to be contaminated with chemical warfare agents. Media such as office flooring, fabrics, paper and wall coverings were spiked with common chemical warfare agents or a complex munitions grade sample of the organophosphorus chemical warfare agent tabun to simulate typical samples. The samples were extracted and analysed in a manner similar to the environmental samples previously studied.

LC-ESI-MS/MS data were acquired during the analysis of an office carpet sample spiked with munitions grade tabun. This type of sample was used during the investigation since terrorist use of chemical warfare agents may involve the use of crude or munitions grade chemical

warfare agent that contains not only the chemical warfare agent but also related co-synthetic, degradation or other products. Extraction and identification of these additional sample components could be helpful in establishing a link between the agent used in the incident and a source, or provide an indication of synthetic route used to prepare the chemical warfare agent. A sample of office carpet was spiked with a munitions grade tabun standard at the $\mu\text{g/g}$ level (approximately 0.5 to 5 $\mu\text{g/g}$ per sample component), extracted and analysed by LC-ESI-MS and LC-ESI-MS/MS. Recoveries ranged between 65% and 92% for tabun and seven related organophosphorus compounds in the aqueous extracts, with tabun being recovered with 75% efficiency from the office carpet.

Figure 7 illustrates LC-ESI-MS and LC-ESI-MS/MS chromatograms obtained during analysis of an aqueous extract of the office carpet spiked with munitions grade tabun. Both ESI-MS and ESI-MS/MS data were obtained for each sample component, with the ESI-MS/MS data being acquired at collision energies that resulted in product ion mass spectra containing both the precursor $[\text{M}+\text{H}]^+$ ion and abundant, structurally informative product ions. Figure 8 illustrates typical product ion mass spectra for tabun and two other related organophosphorus sample components. High resolution data acquired for these and the other related compounds were acquired for identification purposes and have been compiled in Table 3. Errors associated with the mass measurement of the ions were generally less than 0.001 Da, supporting the proposed identities.

The developed method involving aqueous extraction followed by LC-ESI-MS and LC-ESI-MS/MS analysis was successfully applied to the analysis of six different indoor office media contaminated with common chemical warfare agents or a complex munitions grade GA sample. In all cases the spiked components were readily identified in the extracts on the basis of acquired high resolution ESI-MS and/or ESI-MS/MS data, making this method appropriate for these types of sample media and likely applicable to other media that could be collected in support of forensic or CRTI investigations.

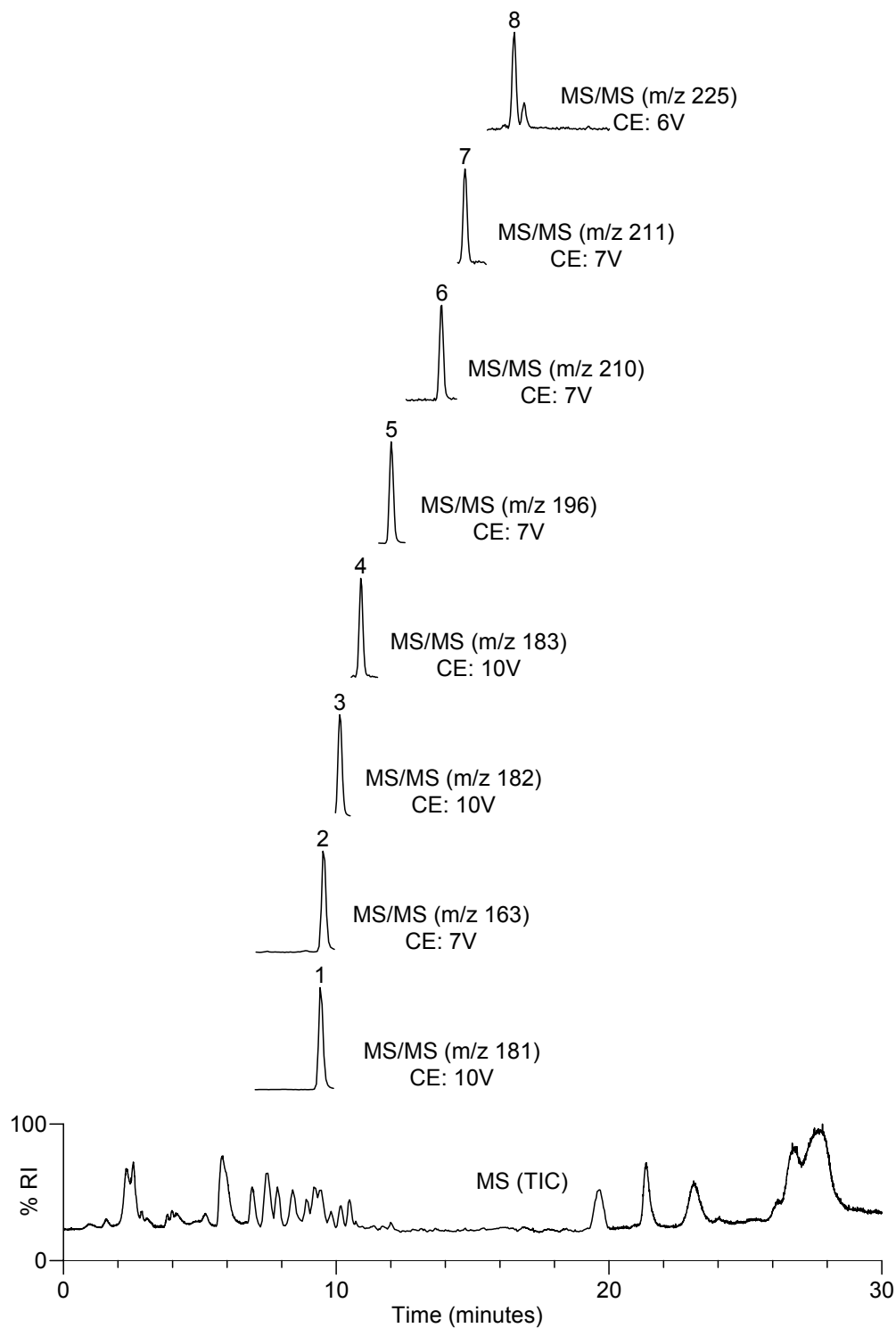


Figure 7. LC-ESI-MS (lowest) and LC-ESI-MS/MS chromatograms (above) of an extract of an office carpet spiked with munitions grade tabun (0.5 – 5 µg/g per component). Components 1 to 8 identified in Table 3. (CE: Collision energy).

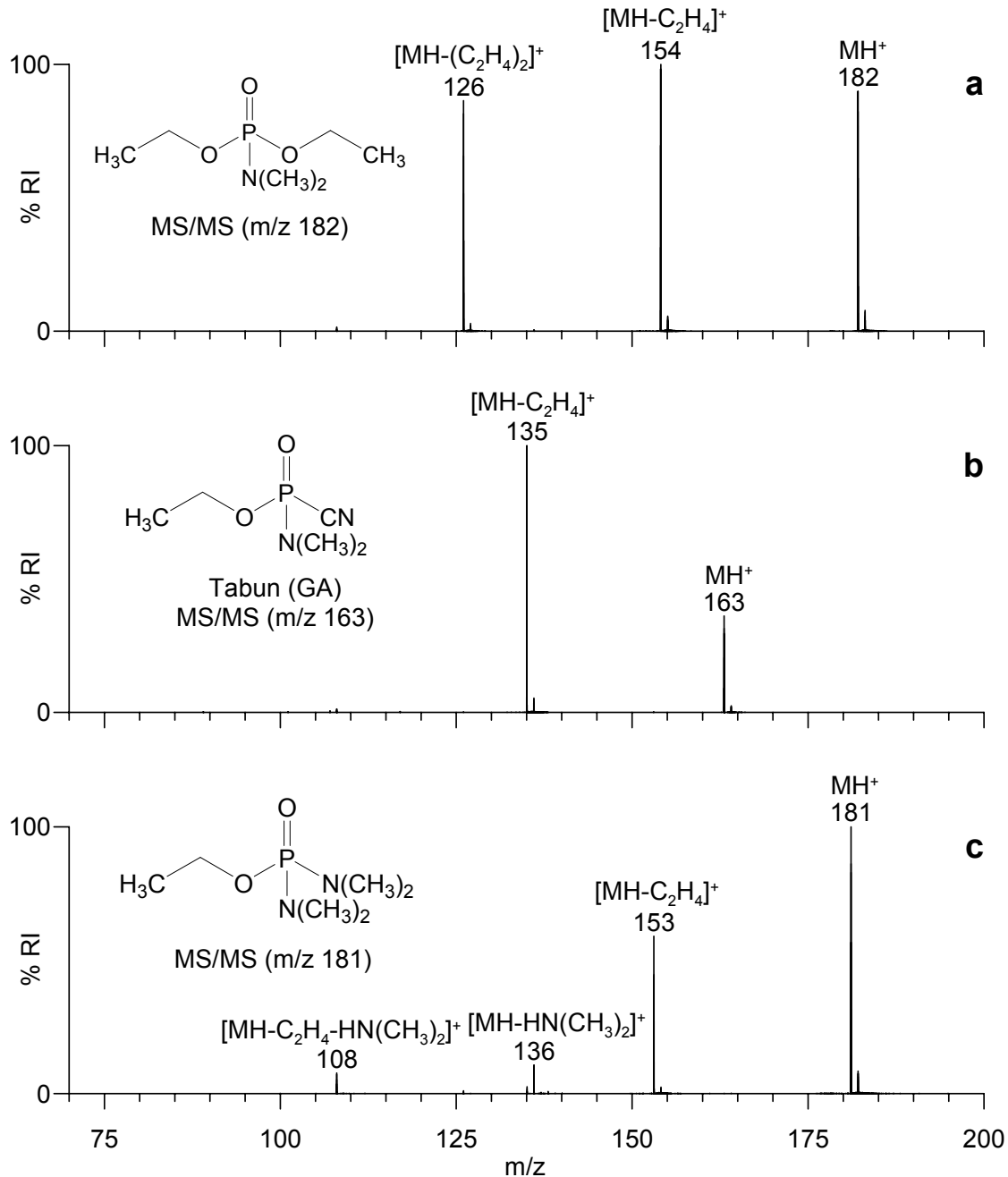


Figure 8. Product ion mass spectra obtained for a) diethyl dimethylphosphoramidate (m/z 182, Collision energy: 10V), b) tabun (m/z 163, Collision energy: 7V) and c) ethyl tetramethylphosphoramidate (m/z 181, Collision energy: 10V) during LC-ESI-MS/MS analysis of an office carpet sample spiked with munitions grade tabun (0.5 to 5 $\mu\text{g/g}$ per component).

Table 3. ESI-MS/MS data acquired for munitions grade tabun components identified in a spiked office carpet extract.

Peak Number ¹	Compound Name	Ion	Observed Mass (Da) ²	Theoretical Mass (Da)	Error (Da)
1	Ethyl tetramethylphosphorodiamidate	MH ⁺	181.1108	181.1106	0.0002
		[MH-C ₂ H ₄] ⁺	153.0795	153.0793	0.0002
		[MH-HN(CH ₃) ₂] ⁺	136.0533	136.0527	0.0006
		[MH- C ₂ H ₄ -HN(CH ₃) ₂] ⁺	108.0215	108.0214	0.0001
2	Ethyl dimethyl-phosphoramidocyanidate (Tabun, GA)	MH ⁺	163.0628	163.0636	0.0008
		[MH-C ₂ H ₄] ⁺	135.0316	135.0323	0.0007
3	Diethyl dimethylphosphoramidate	MH ⁺	182.0950	182.0946	0.0024
		[MH-C ₂ H ₄] ⁺	154.0637	154.0633	0.0004
		[MH-(C ₂ H ₄) ₂] ⁺	126.0322	126.0320	0.0002
4	Triethyl phosphate	MH ⁺	183.0805	183.0786	0.0019
		[MH-C ₂ H ₄] ⁺	155.0470	155.0473	0.0003
		[MH-(C ₂ H ₄) ₂] ⁺	127.0153	127.0160	0.0007
		[MH-(C ₂ H ₄) ₃] ⁺	98.9836	98.9847	0.0011
5	Ethyl isopropyl dimethylphosphoramidate	MH ⁺	196.1109	196.1102	0.0007
		[MH-C ₃ H ₆] ⁺	154.0630	154.0633	0.0003
		[MH-C ₃ H ₆ - C ₂ H ₄] ⁺	126.0327	126.0320	0.0007
6	Diisopropyl dimethylphosphoramidate	MH ⁺	210.1282	210.1259	0.0023
		[MH-C ₃ H ₆] ⁺	168.0790	168.0789	0.0001
		[MH-(C ₃ H ₆) ₂] ⁺	126.0316	126.0320	0.0004
7	Diisopropyl ethyl phosphate	MH ⁺	211.1109	211.1099	0.0010
		[MH-C ₃ H ₆] ⁺	169.0647	169.0629	0.0018
		[MH-(C ₃ H ₆) ₂] ⁺	127.0172	127.0160	0.0012
8	Triisopropyl phosphate	MH ⁺	225.1273	225.1255	0.0018
		[MH-C ₃ H ₆] ⁺	183.0791	183.0786	0.0005
		[MH-(C ₃ H ₆) ₂] ⁺	141.0324	141.0316	0.0008
		[MH-(C ₃ H ₆) ₃] ⁺	98.9842	98.9847	0.0005

¹ Refer to Figure 7.

² Average of scans across the chromatographic peak (lock mass used).

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Appendix A: Open literature analytical methods

DRDC Suffield maintains a comprehensive open literature collection of analytical methods for the detection and identification of chemical warfare agents, their degradation products and related compounds. Paper copies of each paper are held at DRDC Suffield and this comprehensive database of methods continues to be updated regularly using Procite software.

The collection presently contains the following papers, in alphabetical order:

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Ratification of the Chemical Weapons Convention by more than 165 States Parties has reduced the risk of chemical warfare agent use, but there still remains a concern that other parties may make use of these weapons against civilian or military targets. Concerns within the defence and homeland security communities over possible terrorist use as well as the requirements for a verifiable Chemical Weapons Convention, have driven the development of analytical methods such as liquid chromatography-mass spectrometry (LC-MS) for the detection and identification of chemical warfare agents. This paper provides a general overview of chemical warfare agents and analytical methods for their analysis, a focused review on LC-MS applications, a summary of in-house LC-MS methods developed at DRDC Suffield, and a comprehensive bibliography of analytical open literature papers dealing with chemical warfare agent detection and identification.

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